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C-Phosphorylation of *N*-Arylpyrroles

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ABSTRACT: *Phosphorylation of N-arylpyrroles with phosphorus tribromide proceeds regioselectively at the position 2 of the heterocyclic system. A 2-to-3 migration of the dibromophosphino group has been discovered, with its ease depending on the electronic nature of a substituent on the phenyl ring, solvent polarity, and the presence of pyridine hydrobromide in the reaction mixture. Further phosphorylation of 2- and 3-monophosphorylated N-arylpyrroles regioselectively involves the respective positions 4 and 5 of the heterocycle and is governed by the electron-acceptor effect of the phosphorus-containing substituent.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:223–228, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10012

INTRODUCTION

Previously, we showed that phosphorylation of *N*-methylpyrrole with phosphorus tribromide in benzene in the presence of triethylamine takes place regioselectively at position 2 of the heterocyclic system. Interestingly, the resulting 2-dibromophosphino substituent can isomerize to the 3-position in polar solvents [1]. By contrast, *N*-phenylpyrrole is phosphorylated with phosphorus tribromide in benzene nonregioselectively to provide a 1:1 mixture of 2- and 3-*N*-phenyldibromophosphinopyrroles. The dissimilarity in the stereoselectivity of the reaction products impelled us to the study of effects caused by various factors on the phosphorylation regioselectivity and the rate for *N*-arylpyrroles. An interesting challenge was also to ascertain the possibility for the dibromophosphino group in 2-(*N*-arylpyrrolyl)dibromophosphines to undergo a migration.

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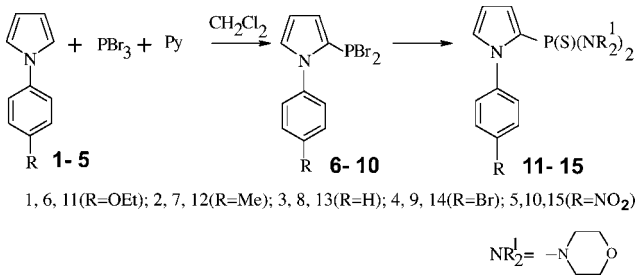
RESULTS AND DISCUSSION

The phosphorylation of *N*-arylpyrroles **1–4** with phosphorus tribromide, carried out in the presence of pyridine in methylene chloride at 20°C, was found to proceed regioselectively (in contrast to the results when benzene was used as a solvent) to generate *N*-aryldibromophosphinopyrroles **6–9** (Scheme 1). *N*-(*p*-Nitrophenyl)pyrrole (**5**) could only be phosphorylated in pyridine medium to furnish the *N*-aryldibromophosphinopyrrole (**10**). Unlike 2-(1-methylpyrrolyl)dibromophosphine, the *N*-aryldibromophosphinopyrroles **6–9** have been isolated in an analytically pure state, as crystalline substances stable in the absence of atmospheric moisture.

Resonances of *N*-aryldibromophosphinopyrroles **6–9** in the ^{31}P NMR spectra are observable in the range $\delta = 122$–126 ppm (Table 1), which suggests that the reactions involve the position 2 of the pyrrole ring, as was proved by us previously [2].

The *N*-aryldibromophosphinopyrroles **6–9** were converted into thioamides **11–15** in high yields (Scheme 1). For thioamide **12**, an informative structure-supporting ^{13}C NMR (Table 2) signal arises from the C^2 atom ($\delta = 112.1$ ppm, $J_{CP} = 150.5$ Hz).



SCHEME 1

Phosphorylation selectivity was significantly influenced by the basicity of the medium and the method of phosphorus tribromide delivery into the reaction mixture. Use of the more basic triethylamine instead of pyridine or addition of undiluted phosphorus tribromide to the reaction mixture results in the formation of a 5–10% yield of the 3-substituted isomer. A material effect on the reaction rate is caused by the nature of a substituent at the para position of the phenyl ring. Thus, the reaction time markedly lengthens with increasing electron acceptor ability of the substituent R in the compound series **1–5** (see Table 3).

Unlike 2-(*N*-methylpyrrolyl)dibromophosphine that completely isomerizes in methylene chloride at 20°C in 2h, solutions of the *N*-aryldibromophosphinopyrroles **6–9** are stable under analogous conditions. Thus, on holding the solutions for 1 month, no more than 5% of 3-substituted isomers can be found in them, as determined by ^{31}P NMR spectroscopy. As 2-(*N*-methylpyrrolyl)dibromophosphine was not isolated in an analytically pure state, it might be supposed that it isomerised because of the presence of the pyridine hydrobromide impurity [1]. It was our intention to verify this suggestion for the *N*-aryldibromophosphinopyrroles **6–9**.

It turned out that, on addition of 1 equiv of pyridine hydrobromide to solutions of the *N*-aryldibromophosphinopyrroles **6–9** in methylene chloride, **6** and **7** underwent isomerization into **16** and **17** (Scheme 2), whereas **8** and **9** did not. A similar situation occurred on aging of the reaction mixtures that resulted from phosphorylation of arylpyrroles **1–4** with phosphorus tribromide in methylene chloride.

^{31}P NMR resonances of dibromophosphines **16** and **17** were observed in the range $\delta = 141$–143 ppm suggesting that the dibromophosphino group had migrated to the position 3 of the pyrrole ring. *N*-aryldibromophosphinopyrroles **16** and **17** furnished thioamides **18** and **19** in high yields (Scheme 2). The signal from C^3 in the ^{13}C NMR (Table 2) spectrum of compound **19** ($\delta = 120.7$ ppm, $J_{CP} = 73.2$ Hz) is indicative of its structure.

The above-presented data provided evidence that a significant effect on the isomerization rate was caused by the nature of a substituent at the nitrogen atom. For instance, the time of isomerization increases notably in going both from the *N*-methyl to

TABLE 1 Yields, Data of Elemental Analysis, and ^{31}P NMR Spectroscopic Characteristics for Compounds **6–27**

					Found % (Calcd %)	
No	*Yield (%)*	*MP (°C)*	*Formula*	*δ_P (CH_2Cl_2)*	*P*	*N*
6	69	oil	$C_{12}H_{12}Br_2NOP$	126.5	8.15 (8.22)	3.58 (3.72)
7	88	oil	$C_{11}H_{10}Br_2NP$	126.0	8.77 (8.93)	3.95 (4.04)
8	84	87	$C_{10}H_8Br_2NP$	125.9	9.35 (9.30)	4.17 (4.21)
9	57	176	$C_{10}H_7Br_3NP$	123.9	7.44 (7.52)	3.21 (3.40)
11	90	83	$C_{20}H_{28}N_3O_3PS$	61.0[a]	7.59 (7.35)	10.02 (9.97)
12	91	157	$C_{19}H_{26}N_3O_2PS$	61.0[a]	7.98 (7.91)	10.81 (10.73)
13	87	131	$C_{18}H_{24}N_3O_2PS$	60.7[a]	8.35 (8.21)	11.35 (11.13)
14	95	207	$C_{18}H_{23}BrN_3O_2PS$	62.3[a]	6.72 (6.79)	9.29 (9.21)
15	74	247	$C_{18}H_{23}N_4O_4PS$	60.3[a]	7.17 (7.33)	13.34 (13.26)
16	64	76	$C_{12}H_{12}Br_2NOP$	143.4	8.14 (8.22)	3.57 (3.72)
17	68	oil	$C_{11}H_{10}Br_2NP$	141.8	9.12 (8.93)	3.95 (4.04)
18	86	105	$C_{20}H_{28}N_3O_3PS$	69.4[a]	7.28 (7.35)	10.16 (9.97)
19	93	157	$C_{19}H_{26}N_3O_2PS$	68.2[a]	7.67 (7.91)	10.81 (10.73)
20	72	127	$C_{20}H_{27}Br_2N_3O_3P_2S$	59.4; 138.7	10.07 (10.13)	7.98 (6.87)
21	64	137	$C_{19}H_{25}Br_2N_3O_2P_2S$	59.3; 137.1	10.81 (10.66)	7.31 (7.23)
22	73	135	$C_{18}H_{23}Br_2N_3O_2P_2S$	59.8; 137.2	10.83 (10.92)	7.53 (7.41)
23	81	198	$C_{18}H_{22}Br_3N_3O_2P_2S$	59.5; 136.8	9.38 (9.59)	6.64 (6.50)
24	93	112	$C_{28}H_{43}N_5O_5P_2S_2$	59.1; 68.2[a]	9.51 (9.45)	10.92 (10.68)
25	86	145	$C_{27}H_{41}N_5O_4P_2S_2$	59.3; 67.8[a]	9.77 (9.90)	11.44 (11.19)
26	88	157	$C_{26}H_{39}N_5O_4P_2S_2$	59.5; 67.9[a]	10.27 (10.13)	11.37 (11.45)
27	93	243	$C_{26}H_{38}BrN_5O_4P_2S_2$	60.0; 67.3[a]	8.71 (8.97)	10.32 (10.14)

[a]Solvent: C_6H_6.

TABLE 2 ^{13}C NMR Data for Compounds **12, 19** in $CDCl_3$: δ, Multiplicity, J (Hz)

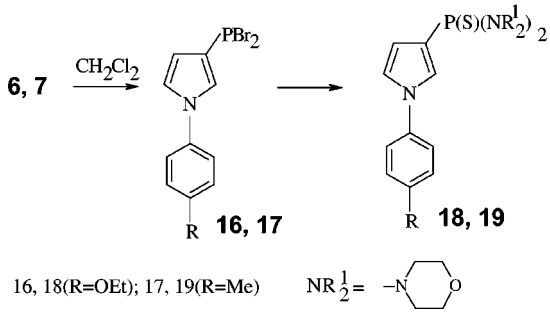
	Het (J_{CP})				*Ar*				
No	*C2*	*C3*	*C4*	*C5*	*C1*	*C2, C6*	*C3, C5*	*C4*	*Others*
12	112.1 d (150.5)	108.9 d (11.9)	130.6 d (7.8)	122.2 t (13.9)	140.1 s	130.8 s	126.3 s	137.0 s	20.5 s (CH_3—Ar); 45.1 s (O—CH_2); 66.0 d (J = 7.5, N—CH_2)
19	137.3 d (45.1)	110.0 d (12.5)	123.5 d (12.8)	120.7 t (73.2)	146.2 s	127.5 s	125.3 s	145.3 s	20.5 s (CH_3—Ar); 45.1 s (O—CH_2); 66.0 d (J = 6.3, N—CH_2)

the *N*-aryl substituted pyrrole and from the *p*-ethoxy (**16**) to the *p*-methyl (**17**) substituted *N*-arylpyrrole (Table 4). For the *N*-aryldibromophosphinopyrroles **8** and **9**, the migration of the dibromophosphino group is so slow that it is of no synthetic value. To be specific, ^{31}P NMR spectroscopic data suggest that the reaction has taken place to the extent of less than 5% during 2 months. The rate of isomerization was also substantially influenced by basicity of the medium. To exemplify, the migration of the dibromophosphino group is considerably slowed down by the presence of an excess of pyridine in the reaction mixture (see Table 4).

The evidence presented in Table 4 leads us to infer that the rearrangement in question is initiated by pyridine hydrobromide and its mechanism may be that shown in Scheme 3.

At the first stage of phosphorylation, the kinetically controlled product **A** is formed, and the equilibrium of **A** with pyrrole and phosphorus tribromide is established in the reaction mixture because of the HBr-induced lability of the C—P bond. The rate of formation of product **B** is much less than that of **A**, but the former is more stable thermodynamically and hence accumulates in the reaction mixture. In support of the assumed mechanism, solutions of isomeric *N*-aryldibromophosphinopyrroles **7** and **17** in methylene chloride were saturated with dry hydrogen bromide at 20°C. The ^{31}P NMR spectrum showed that the peak arising from **7** (δ_P = 126.0 ppm) vanished, as that from phosphorus tribromide (δ_P = 228.3 ppm) appeared and increased. Contrastingly, *N*-aryldibromophosphinopyrrole (**17**) was stable under these conditions.

As with *N*-methylpyrroles, it is possible to successively introduce two phosphorus-containing substituents in an *N*-arylpyrrole molecule. However,



SCHEME 2

an electron-acceptor substituent on phosphorus (a thioamide group) in compounds **11–14** and **18, 19** notably reduces the reactivity of the heterocyclic system to phosphorus tribromide and the reaction can take place only provided pyridine is used both as a solvent and a base. The phosphorylation proceeds regioselectively according to the electron-acceptor effect of the first-introduced substituent. For instance, the substituent residing at the position 2 of the heterocycle (as in amides **11–14**) orients phosphorylation to the position 4 to furnish, in high yields, *N*-aryldibromophosphinopyrroles **20–23** which, in turn, afford thioamides **24–27**. A thioamide substituent at the position 3 of the heterocyclic ring (as in amides **18** and **19**) causes phosphorylation at the position 5 and that results in formation of **28** and**29**, identified by their ^{31}P NMR spectra and characterized by conversion into thioamides **24** and **25** (Scheme 4). The ^{31}P NMR spectra of **20–23** include a singlet peak at δ = 140 ppm, evidently arising from the dibromophosphino group at the position 4

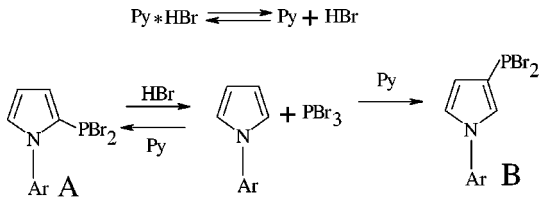
TABLE 3 Time of Reaction for Compounds **6–10**

Product	6	7	8	9	10[a]
Reaction time (h)	0.5	2	8	24	170

[a]In pyridine.

TABLE 4 Relation of Isomerization by Basicity of the Medium

	Product			
	16		*17*	
Pyridine: PBr_3 ratio	1:1	3:1	1:1	3:1
Isomerization time (weeks)	1	3	2	8



SCHEME 3

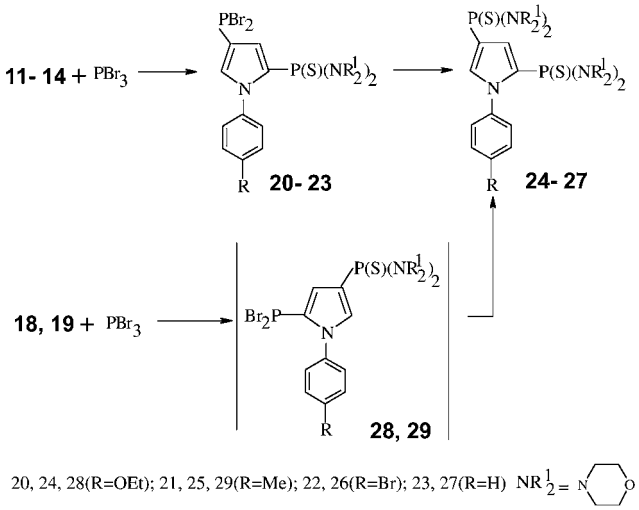
of the pyrrole ring. As regards the reaction mixtures containing dibromophosphines **28** and **29**, an analogous singlet is observed at $\delta = 115$ ppm, suggesting that phosphorylation has involved the position 5.

The phosphorylation rate is essentially governed by the nature of a substituent at the para position of the phenyl ring. Thus, the reaction is materially slowed down with increasing electron acceptor ability of the substituent R in the compounds series **11–14** and in going from **18** to **19** (see Table 5).

An attempt to selectively phosphorylate arylpyrrole **2** with 2 equivalants of phosphorus tribromide failed: The ^{31}P NMR spectrum of the reaction mixture exhibits four signals that can be assigned to isomeric bisdibromophosphines **30–32** contained in the 1:1:0.5 ratio (Scheme 5). These products could not be isolated in an analytically pure state.

EXPERIMENTAL

^{31}P, ^{1}H, and ^{13}C NMR spectra were run on a Varian–VXR 300 spectrometer with TMS being used as an internal standard for ^{1}H and ^{13}C signals, and 85% H_3PO_4 as an external standard for ^{31}P signals (Tables 1, 2, and 6). All manipulations were carried out in anhydrous solvents.



SCHEME 4

TABLE 5 Time of Phosphorylation for Compounds **20–23**, **28**, and **29**

Product	20	21	22	23	28	29
Reaction time (weeks)	2	6	8	20	2	5

General Procedure for Preparation of N-Arylpyrrolyldibromophosphines **6–9**

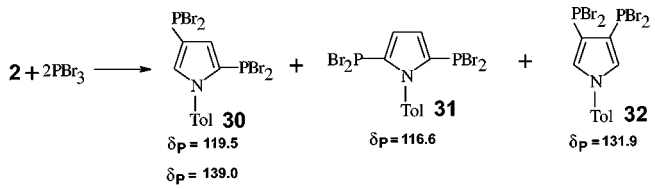
To a stirred solution of each pyrrole **1–4** (0.01 mol) and pyridine (0.01 mol) in methylene chloride (20 ml) was added dropwise a solution of phosphorus tribromide (0.01 mol) in methylene chloride (20 ml) over 10 min. The reaction mixture was allowed to stand at room temperature (see Table 3). After filtration of the mixture, the filtrate was evaporated under reduced pressure. The product was crystallized from octane.

General Procedure for Preparation of Thioamides **11–14**

To a stirred solution of each compound **6–9** (0.01 mol) in benzene (50 ml) was added dropwise a solution of morpholine (0.02 mol) and triethylammine (0.03 mol) in benzene (50 ml) over 10 min; 4 h later sulfur (0.01 mol) was added to the reaction mixture. After heating at 60°C for 2 h, the mixture was filtered and the filtrate was evaporated under reduced pressure. The product was crystallized from octane.

*2-(1-(p-Nitrophenyl))pyrrolyldimorpholinothiophosphonate (***15***)*

To a solution of pyrrole **5** (0.001 mol) in pyridine (10 ml) was added a solution of phosphorus tribromide (0.001 mol) in pyridine (10 ml). After 1 week ($\delta_P = 122.4$ ppm), a solution of morpholine (0.002 mol) and triethylamine (0.003 mol) in benzene (20 ml), followed (0.5 h later) by sulfur (0.001 mol), was added to the reaction mixture. After heating the mixture at 70°C for 2 h, it was allowed to cool and then filtered. The filtrate was evaporated, and the residue was dissolved in methylene chloride (50 ml) and washed with water (2 × 30 ml). After drying the



SCHEME 5

TABLE 6 ^{1}H NMR Data for Compounds **6–27** in $CDCl_3$: δ, Multiplicity, J (Hz)

No	*3-H (2-H)*	*4-H*	*5-H*	*Others*
6	6, 62 dd ($J_{HP} = 3.2$) ($J_{HH} = 2.5$)	6.21 t ($J_{HP} = J_{HH} = 2.5$)	7.31 dd ($J_{HP} = 4.1$) ($J_{HH} = 2.5$)	1.36 t $J_{HH} = 9.0$ (3H, Me); 4.10 k $J_{HH} = 9.0$ (2H, O—CH_2—Me); 6.77 d $J_{HH} = 8.4$ (2H, *m*-Ar); 7.24 d $J_{HH} = 8.4$ (2H, *o*-Ar)
7	6, 67 dd ($J_{HP} = 4.3$) ($J_{HH} = 2.5$)	6.21 t ($J_{HP} = J_{HH} = 2.7$)	7.31 dd ($J_{HP} = 4.3$) ($J_{HH} = 2.5$)	1.98 s (Me); 6.78 d $J_{HH} = 8.1$ (2H, *m*-Ar); 6.97 dd $J_{HH} = 8.1$; $J_{HP} = 2.5$ (2H, *o*-Ar)
8	6.58 m	6.18 t ($J_{HP} = J_{HH} = 3.6$)	7.32 dd ($J_{HP} = 1.5$) ($J_{HH} = 3.6$)	6.91 m (3H, *m*-Ph + *p*-Ph); 7.01 m (2H, *o*-Ph)
9	6, 35 dd ($J_{HP} = 6.3$) ($J_{HH} = 3.0$)	7.06 t ($J_{HP} = J_{HH} = 3.0$)	7.58 dd ($J_{HP} = 6.0$) ($J_{HH} = 3.0$)	7.73 d $J_{HH} = 8.1$ (2H, *m*-Ar); 7.85 d $J_{HH} = 8.1$ (2H, *o*-Ar)
11	6, 79 dd ($J_{HP} = 5.7$) ($J_{HH} = 2.7$)	6, 30 dd ($J_{HP} = 4.2$) ($J_{HH} = 2.7$)	7.17 m	1.34 t $J_{HH} = 9.3$ (3H, Me); 3.0 m (8H, CH_2—N); 3.50 m (8H, CH_2—O); 4.08 k $J_{HH} = 9.3$ (2H, O—CH_2—Me); 6.97 d $J_{HH} = 8.7$ (2H, *m*-Ar); 7.54 d $J_{HH} = 8.7$ (2H, *o*-Ar)
12	6, 81 dd ($J_{HP} = 2.9$) ($J_{HH} = 2.5$)	6.30 t ($J_{HP} = J_{HH} = 2.5$)	6, 99 dd ($J_{HP} = 5.6$) ($J_{HH} = 2.5$)	2.45 s (3H, Me); 3.1 m (8H, CH_2—N); 3.50 m (8H, CH_2—O); 7.21 d $J_{HH} = 8.1$ (2H, *m*-Ar); 7.50 d $J_{HH} = 8.1$ (2H, *o*-Ar)
13	6.82 m	6, 32 dd ($J_{HP} = 3.6$) ($J_{HH} = 2.7$)	7.03 m	3.1 m (8H, CH_2—N); 3.50 m (8H, CH_2—O); 7.41 m (3H, *m*-Ph + *p*-Ph); 7.64 m (2H, *o*-Ph)
14	6.84 m	6, 36 dd ($J_{HP} = 6.0$) ($J_{HH} = 3.0$)	7.26 m	3.0 m (8H, CH_2—N); 3.40 m (8H, CH_2—O); 7.59 d $J_{HH} = 8.1$ (2H, *m*-Ar); 7.66 d $J_{HH} = 8.1$ (2H, *o*-Ar)
15	6.85 m	6, 50 dd ($J_{HP} = 5.1$) ($J_{HH} = 3.0$)	7.20 m	3.20 m (8H, CH_2—N); 3.70 m (8H, CH_2—O); 7.52 d $J_{HH} = 9.0$ (2H, *m*-Ar); 8.32 d $J_{HH} = 9.0$ (2H, *o*-Ar)
16	7.06 m	6.30 t ($J_{HP} = J_{HH} = 3.3$)	6.42 t ($J_{HP} = J_{HH} = 3.3$)	1.44 t $J_{HH} = 9.0$ (3H, Me); 4.07 k $J_{HH} = 9.0$ (2H, O—CH_2—Me); 6.95 d, $J_{HH} = 8.4$ (2H, *m*-Ar); 7.33 d, $J_{HH} = 8.4$ (2H, *o*-Ar)
17	7.48 t ($J_{HP} = J_{HH} = 2.5$)	6.82 t ($J_{HP} = J_{HH} = 2.5$)	7.19 t ($J_{HP} = J_{HH} = 2.5$)	2.41 s (Me); 7.26 s (4H, Ar)
18	7.18 m	6, 31 dd ($J_{HP} = 2.1$) ($J_{HH} = 3.0$)	6.79 m	1.34 t $J_{HH} = 9.6$ (3H, Me); 3.0 m (8H, CH_2—N); 3.50 m (8H, CH_2—O); 4.05 k $J_{HH} = 9.6$ (2H, O—CH_2—Me); 6.97 d, $J_{HH} = 9.0$ (2H, *m*-Ar); 7.55 d, $J_{HH} = 9.0$ (2H, *o*-Ar)
19	7.19 t ($J_{HP} = J_{HH} = 2.5$)	6, 32 dd ($J_{HP} = 6.4$) ($J_{HH} = 2.5$)	6.81 t ($J_{HP} = J_{HH} = 2.5$)	2.36 s (3H, Me); 3.0 m (8H, CH_2—N); 3.40 m (8H, CH_2—O); 7.25 d, $J_{HH} = 8.1$ (2H, *m*-Ar); 7.54 d, $J_{HH} = 8.1$ (2H, *o*-Ar)
20	6.9 m	–	7.38 dd ($J_{HP} = 8.1$) $J_{HH} = 2.1$	1.44 t $J_{HH} = 9.6$ (3H, Me); 3.1 m (8H, CH_2—N); 3.6 m (8H, CH_2—O); 4.08 k $J_{HH} = 9.6$ (2H, O—CH_2—Me); 6.9 m (3H, H^3+ *m*-Ar); 7.47 d $J_{HH} = 8.4$ (2H, *o*-Ar)
21	6, 93 dd ($J_{HP} = 5.0$) ($J_{HP} = 2.1$)	–	6, 32 d ($J_{HP} = 1.5$)	2.44 s (3H, Me); 3.4 m (8H, CH_2—N); 3.9 m (8H, CH_2—O); 7.27 s (4H, Ar)
22	6.9 m	–	6, 35 d ($J_{HP} = 1.5$)	3.2 m (8H, CH_2—N); 3.6 m (8H, CH_2—O); 7.4 m (3H, *m*-Ph + *p*-Ph); 7.6 m (2H, *o*-Ph)
23	6, 98 dd ($J_{HP} = 4.0$) ($J_{HP} = 2.1$)	–	6, 39 d ($J_{HP} = 1.5$)	3.2 m (8H, CH_2—N); 3.6 m (8H, CH_2—O); 7.59 d $J_{HH} = 8.4$ (2H, *m*-Ar); 7.66 d $J_{HH} = 8.4$ (2H, *o*-Ar)
24	6.9 m	–	7.35 t ($J_{HP} = J_{HP} = 8.7$)	1.43 t $J_{HH} = 10.0$ (3H, Me); 3.0 m (8H, CH_2—N); 3.6 m (8H, CH_2—O); 4.06 k $J_{HH} = 10.0$ (2H, O—CH_2—Me); 6.9 m (3H, H^3+ *m*-Ar); 7.49 d, $J_{HH} = 8.1$ (2H, *o*-Ar)

(Continued)

TABLE 6 Continued

No	*3-H (2-H)*	*4-H*	*5-H*	*Others*
25	6.93 t ($J_{HP} = J_{HP} = 5.0$)	–	7.44 d ($J_{HP} = 4.5$)	2.37 s (3H, Me); 3.0 m (8H, CH_2—N); 3.50 m (8H, CH_2—O); 7.28 d $J_{HH} = 7.2$ (2H, *m*-Ar); 7.50 d $J_{HH} = 7.2$ (2H, *o*-Ar)
26	6, 98 dd ($J_{HP} = 6.1$) ($J_{HP} = 3.0$)	–	7.55 d ($J_{HP} = 6.5$)	3.1 m (8H, CH_2—N); 3.5 m (8H, CH_2—O); 7.5 m (3H, *m*-Ph + *p*-Ph); 7.9 m (2H, *o*-Ph)
27	6, 96 dd ($J_{HP} = 4.0$) ($J_{HP} = 2.1$)	–	7.59 d ($J_{HP} = 6.2$)	3.2 m (8H, CH_2—N); 3.6 m (8H, CH_2—O); 7.69 d $J_{HH} = 8.1$ (2H, *m*-Ar); 7.92 d $J_{HH} = 8.1$ (2H, *o*-Ar)

solution with sodium sulfate, it was evaporated and the residue was washed with benzene on a filter.

General Procedure for Preparation of N-Arylpyrrolyldibromophosphines **16** *and* **17**

Method A. To a stirred solution of each pyrrole **1** and **2** (0.01 mol) and pyridine (0.01 mol) in methylene chloride (20 ml) was added dropwise a solution of phosphorus tribromide (0.01 mol) in methylene chloride (20 ml) over 10 min. The reaction mixture was allowed to stand at room temperature (see Table 4). After filtration of the mixture, the filtrate was evaporated under reduced pressure. The product was crystallized from octane.

Method B. To a stirred solution of each compound **6** and **7** (0.01 mol) in methylene chloride (50 ml) was poured pyridine hydrobromide (0.01 mol) and the mixture was allowed to stand at room temperature (see Table 4). After filtration of the mixture, the filtrate was evaporated under reduced pressure. The product was crystallized from octane.

General Procedure for Preparation of Thioamides **18** *and* **19**

To a stirred solution of each compound **16** and **17** (0.01 mol) in benzene (50 ml) was added dropwise a solution of morpholine (0.02 mol) and triethylamine (0.03 mol) in benzene (50 ml) over 10 min; 4 h later sulfur (0.01 mol) was added to the reaction mixture. After heating at 60°C for 2 h, the mixture was filtered and the filtrate was evaporated under reduced pressure. The product was crystallized from octane.

General Procedure for Preparation of N-Arylpyrrolyldibromophosphines **20–23**

To a stirred solution of thioamide **11–14** (0.01 mol) in pyridine (50 ml) was added dropwise a solution of phosphorus tribromide (0.01 mol) in pyridine (10 ml). The reaction mixture was allowed to stand at room temperature (see Table 5). After filtration of the mixture, the filtrate was evaporated under reduced pressure. The product was purified by precipitation from benzene with hexane.

General Procedure for Preparation of Each bis-Thioamide **24–27**

To a stirred solution of each compound **20–23** (0.01 mol) in benzene (50 ml) was added dropwise a solution of morpholine (0.02 mol) and triethylamine (0.03 mol) in benzene (50 ml) over 10 min; 4 h later sulfur (0.01 mol) was added to the reaction mixture. After heating at 60°C for 2 h, the mixture was filtered and the filtrate was evaporated under reduced pressure. The product was crystallized from ethanol.

Preparation of bis-Thioamides **24, 25** *from Thioamides* **18, 19**. To a stirred solution of each thioamide **18** and **19** (0.01 mol) in pyridine (50 ml) was added dropwise a solution of phosphorus tribromide (0.01 mol) in pyridine (10 ml). The reaction mixture was allowed to stand at room temperature (see Table 3), and then a solution of morpholine (0.02 mol) and triethylamine (0.03 mol) in benzene (20 ml), followed (2 h later) by sulfur (0.01 mol) was added to it. After heating the mixture at 70°C for 4 h, it was allowed to cool and then filtered. The filtrate was evaporated under reduced pressure and the product was crystallized from ethanol.

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